

Modeling the Physical Multi-Phase Interactions of HNO_3 Between Snow and Air on the Antarctic Plateau (Dome C) and coast (Halley)

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Nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) emissions from nitrate (NO_3^-) photolysis in snow affect the oxidising capacity of the lower troposphere especially in remote regions of the high latitudes with low pollution levels. The porous structure of snowpack allows the exchange of gases with the atmosphere driven by physicochemical processes, and hence, snow can act as both source and sink of atmospheric chemical trace gases. Current models are limited by poor process understanding and often require tuning parameters. Here, two multi-phase physical models were developed from first principles constrained by observed atmospheric nitrate, HNO_3 , to describe the air-snow interaction of nitrate. Similar to most of the previous approaches, the first model assumes that below a threshold temperature, T_o , the air-snow grain interface is pure ice and above T_o , a disordered interface (DI) emerges assumed to be covering the entire grain surface. The second model assumes that Air-Ice interactions dominate over the entire temperature range below melting and that only above the eutectic temperature, liquid is present in the form of micropockets in grooves. The models are validated with available year-round observations of nitrate in snow and air at a cold site on the Antarctica Plateau (Dome C, $75^\circ 06'S$, $123^\circ 33'E$, 3233 m a.s.l.) and at a relatively warm site on the Antarctica coast (Halley, $75^\circ 35'S$, $26^\circ 39'E$, 35 m a.s.l.). The first model agrees reasonably well with observations at Dome C ($\text{Cv}(\text{RMSE}) = 1.34$), but performs poorly at Halley ($\text{Cv}(\text{RMSE}) = 89.28$) while the second model reproduces with good agreement observations at both sites without any tuning ($\text{Cv}(\text{RMSE}) = 0.84$ at both sites). It is therefore suggested that air-snow interactions of nitrate in the winter are determined by non-equilibrium surface adsorption and co-condensation on ice coupled with solid-state diffusion inside the grain. In summer, however, the air-snow exchange of nitrate is mainly driven by solvation into liquid micropockets following Henry's law with contributions to total NO_3^- concentrations of 75% and 80% at Dome C and Halley respectively. It is also found that liquid volume of the snow grain and air-micropocket partitioning of HNO_3 are sensitive to total solute concentration and pH. In conclusion, the second model can be used to predict nitrate concentration in surface snow over the entire range of environmental conditions typical for Antarctica and forms a basis for parameterisations in regional or global atmospheric chemistry models.